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Rapid quenching by the Taylor wire technique

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The Taylor method for obtaining fine wires has been used to investigate glass formation at high cooling rates. The rates of 10^3 to 10^5 K sec^{-1} obtained by this process lie between those associated with splat cooling and bulk quenching methods. The formation of novel oxide and sulphate glasses is used to both illustrate the scope of the Taylor technique and to emphasize its major disadvantage – contamination of the core material by the glass sheath.

1. Introduction

Refinements to the Taylor [1, 2] process for obtaining metallic micro-filaments by drawing a duplex fibre from a glass tube containing the molten metal have been described by many authors [3–9]. Interest has previously centred on the micro-wire forming potential of the process.

In this paper we show that the cooling rates obtained in conventional glass fibre drawing processes can be applicable in the production of Taylor wires. These cooling rates $\sim 10^5$ to 10^3 K sec^{-1} are of the same order as required for the quenching of some glassy metal compositions.

In addition we extend the scope of the Taylor process to include non-metal systems as the core material, and use the high cooling rates to investigate novel glass forming systems.

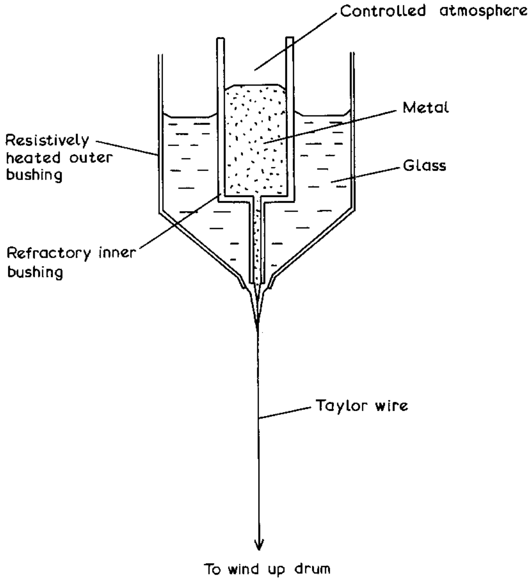

Figure 1 Schematic representation of double bushing.

2. Experimental procedures

2.1. Continuous fibre formation

The basic concept of the Taylor process has been combined with glass fibre double bushing techniques [10–12] to give the capability of continuously producing glass sheathed metallic micro-filament. Fig. 1 shows a schematic diagram of this technique. For any particular metal/glass combination the relative bushing tip diameters and positions may be varied to obtain the desired core/sheath ratio in the final filament. To obtain void-free cores the criteria instanced by Manfrè *et al.* [7] for temperature profiles in the fibre-forming zone must be maintained. The top view of a trial bushing is shown in Fig. 2. Molten copper is held in an alumina sheath and the surrounding "E" glass is held in a resistively heated platinum bushing. On a small scale the atmosphere above the molten metal may be crudely controlled by covering the surface with powdered graphite.

2.2. Small scale preparation

Sufficient material for tests of glass forming ability can be obtained by merely stretching by hand the cored glass preform, which itself is formed by inserting the proposed core material

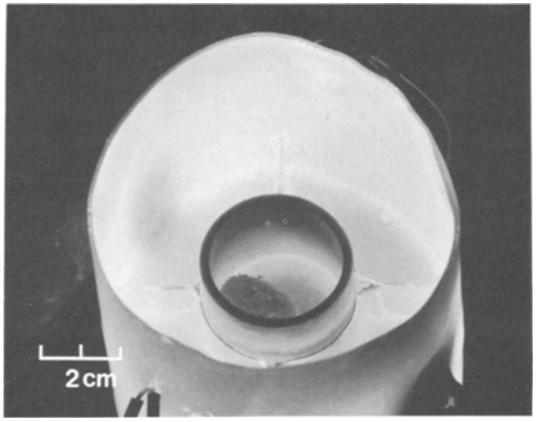

Figure 2 Top view of double bushing.

in the form of rod, powder, or melt, into a glass tube. The advantage of this technique is that it readily gives tapered fibres whose diameter varies by 3 orders of magnitude (2 mm to 2 μm) from one end to the other.

2.3. Testing procedures

Specimen cores were investigated for crystallinity using polarizing optical microscopy, and Debye–Scherrer X-ray techniques (Fig. 3). SEM micrographs were obtained for investigating fracture surfaces across the fibres (Fig. 4) and the microstructure of crystalline metal cores.

3. Results and discussion

3.1. Fibre cooling rates

The experimental and theoretical cooling profiles for commercial glass fibres are well established. From the temperature profiles for continuous filament production of E glass given by Manfrè [13] cooling rates of $0.4 \times 10^4\,\mathrm{K\,sec^{-1}}$ and $6 \times 10^4\,\mathrm{K\,sec^{-1}}$ can be obtained for fibres of 104 and 18 μm diameter respectively.

Though both convective and radiative processes contribute to the cooling of a fibre during the drawing process, for regions after the initial forming zone the convective process dominates. Below the forming zone a convective cooling coefficient of $0.15\,k/r$ may be used to estimate the cooling rate [14] where r is the fibre radius (in m) and k is an appropriate thermal conductivity of air. For typical conditions this coefficient is $0.008/r\,\mathrm{W\,m^{-2}\,K^{-1}}$, giving:

$$\text{Cooling rate} = \frac{0.016 \times \Delta T}{r^2 \times \rho \times C}\,\mathrm{K\,sec^{-1}} \qquad (1)$$

For a 20 μm diameter fibre at 800 K above ambient the calculated convective heat transfer rate is $640\,\mathrm{kW\,m^{-2}}$ (over 10 times greater than the expected radiative contribution). Considering glass of density (ρ) $2300\,\mathrm{kg\,m^{-3}}$ and specific heat (C) $1400\,\mathrm{J\,kg^{-1}\,K^{-1}}$ Equation 1 gives a cooling rate of $4 \times 10^4\,\mathrm{K\,sec^{-1}}$. The equivalent rate for a 10 μm diameter fibre is $1.6 \times 10^5\,\mathrm{K\,sec^{-1}}$.

With a metallic core to the fibre the convective cooling coefficient is unchanged. Differences in cooling rate are due to the altered heat capacity of the fibre, the $r^2\rho C$ term of Equation 1 becoming:

$$r^2(\rho C)_{\text{glass}} + r^2_{\text{core}}\{(\rho C)_{\text{core}} - (\rho C)_{\text{glass}}\} \equiv r^2(\rho' C') \qquad (2)$$

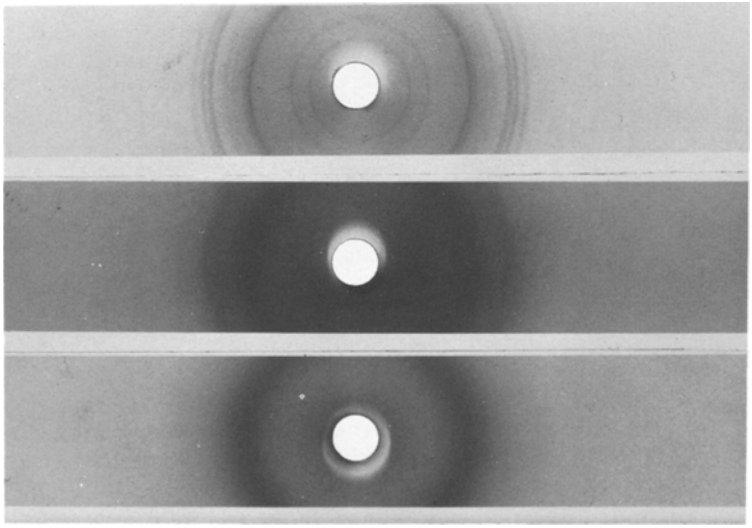

Figure 3 Debye–Scherrer photographs of: top, crystalline potassium–calcium sulphate; middle, partially crystalline potassium–manganese sulphate; bottom, glassy vanadium pentoxide.

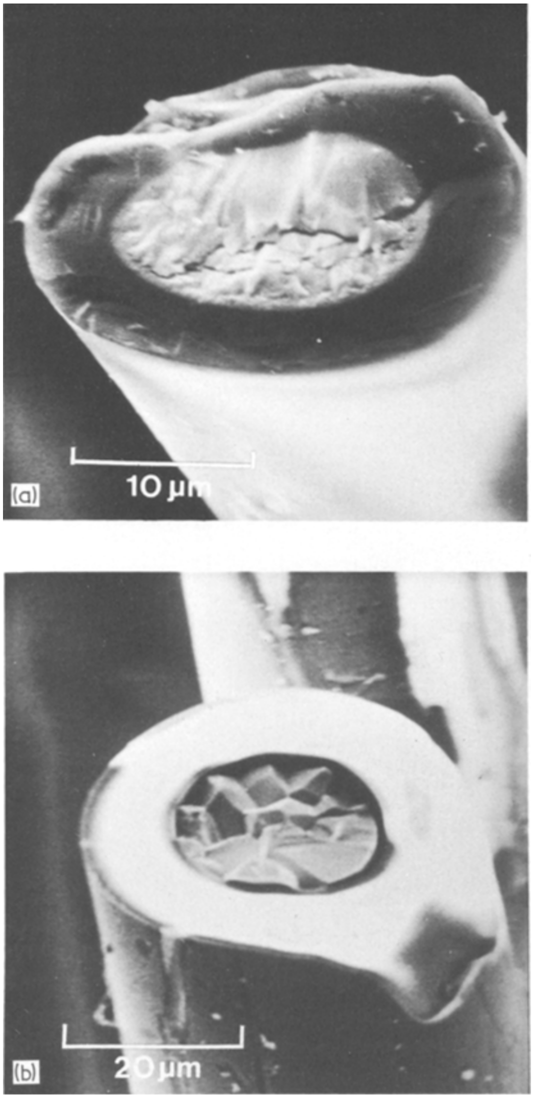

Figure 4 Fracture surfaces across Taylor wires containing cores of (a) glassy lead oxide, (b) crystalline silver chloride.

where the primed constants are the effective overall values calculated for any particular core–sheath diameter ratio.

The product of density and specific heat values, tabulated for a range of materials in Table I, shows remarkable constancy. For an extreme range of core materials the cooling rate will vary by less than 20% – i.e. the fibre diameter is the dominant factor determining the cooling rate.

TABLE I Density and specific heat values

Substance	ρ	C	ρC	$\rho' C'$
Glass	2500	670	1.67×10^6	1.67×10^6
Al	2700	926	2.50×10^6	1.88×10^6
PbO	9500	200	1.90×10^6	1.73×10^6
Na_2SO_4	2680	846	2.27×10^6	1.82×10^6

Values in SI Units at 300 K. $\rho' C'$ calculated for $r_{\text{core}} = 0.5 \times r$

For simplified Taylor wire preparation methods (Section 2.1) the formed fibre remains almost stationary and the cooling rates are lower than those indicated above. The absence of the forced draught cooling gives a fibre cooling rate that is dependent on surface area and sensitive to the local air currents. However, for a tapered fibre this still means that a range of $\sim 10^3$ in cooling rate may be obtained along its length, leading to the frequent occurrence of fibres whose cores have a marked transition from crystalline to glass. The diameter at which this transition occurs is a simple measure of the glass forming ability of the system, though the absolute cooling rate is not known.

3.2. Experimental cooling rate

Taylor wires were hand-drawn with an Al–Cu eutectic alloy (67.0 wt% Al) as the core material in a borosilicate sheath. Fig. 5 shows the typical lamellar microstructure. For a 36 μm diameter fibre (core diameter = 18 μm) the inter-lamellar spacing is in the range 0.2 to 0.4 μm. Using the method of Burden and Jones [15], but modified

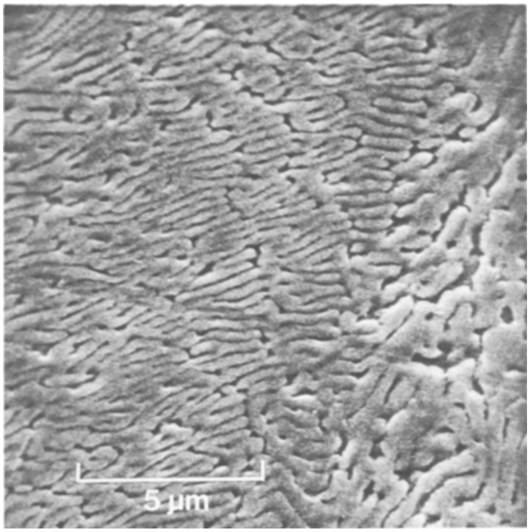

Figure 5 Microstructure shown by Al–Cu Al_2 eutectic (KOH etch).

for a cored fibre rather than a splat, the cooling rate is given by:

$$\text{Cooling rate} = \frac{2r_c\rho_c L_c R}{r^2(\rho' C')} \qquad (3)$$

where L is the latent heat of fusion and R the crystal growth velocity at the core perimeter. Values with a c subsript refer to the core and primed values are defined as in Equation 2. Using the quoted [15] values for Cu–Al, a spacing of 0.3 μm with a corresponding crystal growth velocity of 1×10^{-3} m sec^{-1} indicates a fibre cooling rate of 4×10^4 K sec^{-1}. This compares with a value of 1×10^4 K sec^{-1} calculated from Equations 1 and 2 for a continuously drawn filament at the crystallization temperature (548° C).

3.3. Vitrification studies

3.3.1. Oxides

Taylor wires were drawn from a sodium borosilicate glass with PbO, Bi_2O_3 and V_2O_5 cores. All three systems gave glassy cores for relatively thick (50 μm diameter) fibres. V_2O_5 is the only one of the three that is known to form a glass by splat cooling methods [16]. In the Taylor process the glass forming ability of the core material has been enhanced by contamination from reaction with the sheath. Fig. 6 shows a microprobe analysis trace across the composite lead oxide fibre. The silica concentration in the core of 1.4 wt% is less than is required to make a bulk glass in the PbO–SiO_2 system, but it clearly shows that by the Taylor method we are not investigating the characteristics of pure lead oxide. Similarly, analysis of the Bi_2O_3 glass showed 2.2 wt% SiO_2, 0.7 wt% Al_2O_3 and 0.4 wt% Na_2O, and the V_2O_5 glass contained 0.6 wt% SiO_2.

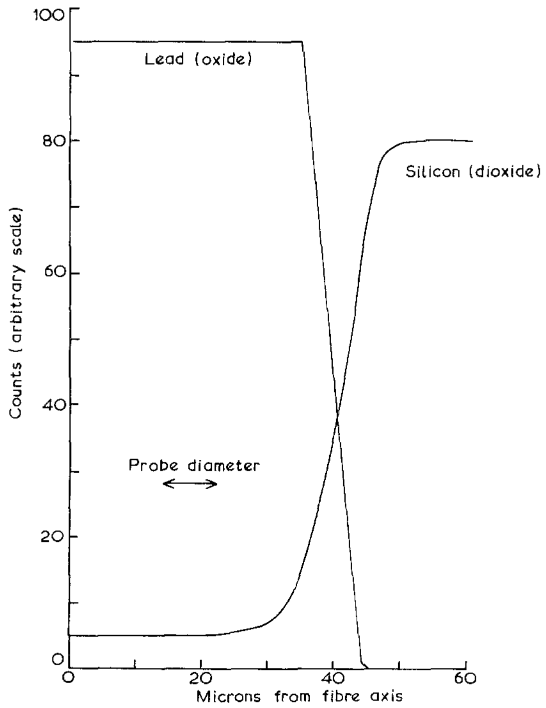

Figure 6 Microprobe analysis trace across lead oxide cored Taylor wire.

There are conflicting reports of the glass forming ability of Bi_2O_3 [16, 17]. However, a 20 mg microfurnace technique found [18] 91 wt% to be the maximum Bi_2O_3 content for a Bi_2O_3–SiO_2 glass. The higher cooling rates of the Taylor process have allowed the glass forming range to be extended to higher Bi_2O_3 content.

The PbO, Bi_2O_3 and V_2O_5 glass cores devitrified on being held at 500° C for 30 min. DTA traces for the PbO and V_2O_5 glasses exhibited crystallization exotherms at 330° C and 310° C respectively. In comparison pure splat cooled amorphous V_2O_5 gives an exotherm at 216° C [19].

3.3.2. Sulphates

Previously reported glasses in the sulphate system include $KHSO_4$ [20] and a series of compounds in the system Tl_2SO_4–K_2SO_4–$ZnSO_4$–$CuSO_4$, [21] the latter series being made on a 5 g scale, with no glasses found in the corresponding Li_2SO_4 and Na_2SO_4 systems. By the Taylor technique the known glass forming system of equimolar K_2SO_4–$ZnSO_4$ formed a glass on merely sucking the molten salt into a cold glass tube, and an equimolar Na_2SO_4–$ZnSO_4$ would form a glass when drawn into fibres of less than 13 μm diameter. At a similar fibre diameter an equimolar K_2SO_4–$MnSO_4$ mixture also formed a glass. No glass could be formed in the K_2SO_4–(Ca, Mg)SO_4 system even with fibre diameters of 2 μm.

3.3.3. Halides

A glass was formed for very fine fibres in the fluoride system (PbF_2:AlF_3:MgF_2, 45:34:21 mol%). This glass contains neither of the usual fluoride glass formers, BeF_2 and HF [22], but resembles those found by Sun [23, 24] in which AlF_3 is thought to behave as a network former.

3.4. Core contamination

In Section 3.3.1 examples are given of contamination of the core by the sheath material. This phenomena is not limited to cores of oxide materials which might be expected to be compatible to some extent with the glass sheath. The contamination can also occur in the metallic systems for which the process is traditionally used.

The analysis of aluminium which had a silicon content of 1.3 kg m^{-3} before drawing showed 4 kg m^{-3} of silicon when hand drawn into a 20 μm diameter Taylor wire in a borosilicate glass sheath.

4. Conclusions

The Taylor process is a convenient method of subjecting materials to cooling rates in the range 10^3 to 10^5 K sec^{-1}. Sufficient material can be obtained for analysis by normal optical or microanalysis techniques. Theoretical expressions for cooling rates derived for conventional glass fibres can be extended to cored fibres and give results within an order of magnitude of those obtained experimentally for hand-drawn Taylor wires.

The major disadvantage of the process is the high probability of chemical reaction between the core and sheath materials, leading to contamination of the core. Thus, whenever this process is used, the glass forming ability of a system must be related to both the cooling rate and an analysis of the final core material.

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